

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
13 June 2002 (13.06.2002)

PCT

(10) International Publication Number
WO 02/47119 A2

- (51) International Patent Classification⁷: **H01L**
- (21) International Application Number: PCT/US01/46877
- (22) International Filing Date: 4 December 2001 (04.12.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
09/731,534 6 December 2000 (06.12.2000) US
- (71) Applicant: **THE REGENTS OF THE UNIVERSITY OF CALIFORNIA** [US/US]; Los Alamos National Laboratory, LC/IP, MS A187, Los Alamos, NM 87545 (US).
- (72) Inventors: **ARENDET, Paul, N.**; 411 Richard Court, Los Alamos, NM 87544 (US). **FOLTYN, Stephen, R.**; 1 Mariposa Court, Los Alamos, NM 87544 (US). **GROVES, James, R.**; 2426-A 35th Street, Los Alamos, NM 87544 (US). **HOLESENGER, Terry, G.**; 2783-A Walnut Street, Los Alamos, NM 87544 (US). **JIA, Quanxi**; 832 Kristi Lane, Los Alamos, NM 87544 (US).
- (74) Agents: **COTTRELL, Bruce, H.** et al.; Los Alamos National Laboratory, LC/IP, MS A187, Los Alamos, NM 87545 (US).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— *without international search report and to be republished upon receipt of that report*
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: HIGH TEMPERATURE SUPERCONDUCTING THICK FILMS FIELD OF THE INVENTION

(57) Abstract: An article including a substrate, a layer of an inert oxide material upon the surface of the substrate, (generally the inert oxide material layer has a smooth surface, i.e., a RMS roughness of less than about 2 nm), a layer of an amorphous oxide or oxynitride material upon the inert oxide material layer, a layer of an oriented cubic oxide material having a rock-salt-like structure upon the amorphous oxide material layer is provided together with additional layers such as at least one layer of a buffer material upon the oriented cubic oxide material layer or a HTS top-layer of YBCO directly upon the oriented cubic oxide material layer. With a HTS top-layer of YBCO upon at least one layer of a buffer material in such an article, J_c 's of 1.4×10^6 A/cm² have been demonstrated with projected I_c 's of 210 Amperes across a sample 1 cm wide.

WO 02/47119 A2

HIGH TEMPERATURE SUPERCONDUCTING THICK FILMS FIELD OF THE INVENTION

The present invention relates to high temperature superconducting thick films on polycrystalline substrates with high J_c 's and I_c 's and to structural template articles for subsequent deposition of an oriented film, e.g., of superconducting thick films. This invention is the result of a contract with the United States Department of Energy (Contract No. W-7405-ENG-36). The government has certain rights to this invention.

BACKGROUND OF THE INVENTION

One process in the production of coated conductors (superconductive tapes or films) has been referred to as a thick film process where the thickness of the superconductive layer is generally at least one micron in thickness. In the thick film process, it has been shown that YBCO thin films on single crystal substrates can achieve critical current density (J_c) values of over 10^6 amperes per square centimeter (A/cm^2) at 77 K. The use of polycrystalline substrates other than single crystals was desired. For amorphous or polycrystalline substrates, the use of a suitable buffer layer to provide the necessary structural template was developed. For example, a YSZ buffer layer has been deposited by use of ion beam assisted deposition (IBAD) in which a YSZ layer is deposited in combination with irradiation from an ion beam directly on a substrate during the deposition. For example, both Iijima et al., U.S. Patent No. 5,650,378 and Russo et al., U.S. Patent No. 5,432,151 have demonstrated deposition of in-plane textured YSZ buffer layers with IBAD, leading to YBCO thin films having excellent superconducting properties. Arendt et al., U.S. Patent No. 5,872,080 described a coated conductor having the structure YBCO/ Y_2O_3 /YSZ/ Al_2O_3 /Ni alloy with a high critical current density (J_c) of about $1 \times 10^6 A/cm^2$ and a high transport critical current (I_c) of from about 100 to about 200 A/cm. The in-plane textured YSZ of Arendt et al. was more highly aligned than that obtained by either Iijima or Russo. While the current was satisfactory, the deposition of the YSZ layer was considered too slow for commercial production.

In WO 99/25908, thin films of a material having a rock salt-like structure were deposited by IBAD upon amorphous substrate surfaces. Among the materials with a rock salt-like structure was magnesium oxide (MgO). In comparison to the deposition of YSZ, MgO can be rapidly deposited (about 100 times faster) through an IBAD process. The

structures of WO 99/25908 included, e.g., YBCO/Y₂O₃/YSZ/MgO/MgO(IBAD)/Si₃N₄/Ni alloy with a NiO layer in between the YSZ layer and the MgO layer in most instances.

Despite the improvement in processing speeds, the structures of WO 99/25908 had I_c's of only about 50 to about 75 A/cm. In addition, at the elevated processing temperatures

5 needed to form the superconductive layer, the silicon nitride layer reacts with other materials in the system.

Thus, further improvements in the structure and resultant properties of coated conductors have been desired. After extensive and careful investigation, improvements have been found in the preparation of superconducting films on polycrystalline substrates
10 such as flexible polycrystalline metal substrates.

It is an object of the present invention to provide superconducting films, especially YBCO superconducting films, on polycrystalline substrates such resultant articles demonstrating properties such as high J_c's and I_c's.

It is another object of the present invention to provide structural template articles for
15 subsequent deposition of oriented films, e.g., superconducting films, especially YBCO superconducting films.

SUMMARY OF THE INVENTION

To achieve the foregoing and other objects, and in accordance with the purposes of the present invention, as embodied and broadly described herein, the present invention
20 provides an article including a substrate, a layer of an inert oxide material upon the surface of the substrate, a layer of an amorphous oxide or oxynitride material upon the inert oxide material layer, and a layer of an oriented cubic oxide material having a rock-salt-like structure upon the amorphous oxide or oxynitride material layer. In a preferred embodiment, the article is a superconductive article and further includes at least one layer
25 of a buffer material upon the oriented cubic oxide material and a top-layer of a HTS material upon the buffer material layer.

In another embodiment of the invention, the article further includes a homo-epitaxial layer of the oriented cubic oxide material having a rock-salt-like structure between an initially deposited oriented cubic oxide material layer and a first buffer material layer.

In another embodiment of the invention, the present invention provides an article including a substrate, a layer of an amorphous oxide or oxynitride material upon the substrate, and a layer of an oriented cubic oxide material having a rock-salt-like structure upon the amorphous oxide or oxynitride material layer. In another preferred embodiment, the article is a superconductive article and further includes at least one layer of buffer material upon the oriented cubic oxide material layer and a top-layer of a HTS material upon the buffer material layer.

The present invention also provides a thin film template structure including a flexible polycrystalline metal substrate, a layer of an inert oxide material upon the surface of the flexible polycrystalline metal substrate, a layer of an amorphous oxide or oxynitride material upon the inert oxide material layer, and, a layer of an oriented cubic oxide material having a rock-salt-like structure upon the amorphous oxide or oxynitride material layer. In alternative embodiments, additional layers, e.g., buffer layers can be added onto the layer of an oriented cubic oxide material. Such thin film template structures of the present invention are useful for subsequent epitaxial thin film deposition.

The present invention also provides a thin film template structure including a flexible polycrystalline metal substrate, a layer of an inert oxide material upon the surface of the flexible polycrystalline metal substrate, and a layer of an amorphous oxide or oxynitride material upon the inert oxide material layer. Such thin film template structures of the present invention are useful for subsequent inclined substrate deposition.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 shows an illustrative structure of a superconductive article in accordance with the present invention.

DETAILED DESCRIPTION

The present invention is concerned with high temperature superconducting wire or tape and the use of high temperature superconducting thick films to form such wire or tape. The present invention is further concerned with the preparation of structural template articles for the subsequent deposition of oriented films, e.g., superconducting thick films or other materials where orientation is desirable.

In the present invention, the high temperature superconducting (HTS) material is generally YBCO, e.g., $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{14+x}$, or $\text{YBa}_2\text{Cu}_4\text{O}_8$, although other minor variations of this basic superconducting material, such as use of other rare earth metals as a substitute for some or all of the yttrium as is well known, may also be used. Other
5 superconducting materials such as bismuth and thallium based superconductor materials may also be employed. $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is preferred as the superconducting material.

In the present invention, the initial or base substrate can be, e.g., any polycrystalline material such as a metal or a ceramic such as polycrystalline aluminum oxide or polycrystalline yttria-stabilized zirconia (YSZ). Preferably, the substrate can be a
10 polycrystalline metal such as nickel. Alloys including nickel such as various Hastelloy metals, Haynes metals and Inconel metals are also useful as the substrate. The metal substrate on which the superconducting material is eventually deposited should preferably allow for the resultant article to be flexible whereby superconducting articles (e.g., coils, motors or magnets) can be shaped. As such a metal substrate can have a rough surface, it
15 can be mechanically polished, electrochemically polished or chemically mechanically polished to provide a smoother surface. Alternatively, the desired smoothness for subsequent depositions can be provided by the first coating layer, i.e., an inert oxide material layer.

Whether the metal substrate is polished or not, a layer of an inert oxide material can be
20 deposited upon the base substrate. By "inert" is meant that this oxide material does not react with the base substrate or with any subsequently deposited materials. Examples of suitable inert oxide materials include aluminum oxide (Al_2O_3), erbium oxide (Er_2O_3), yttrium oxide (Y_2O_3), and yttria-stabilized zirconia (YSZ). The inert oxide layer can be deposited on the base substrate by pulsed laser deposition, e-beam evaporation, sputtering
25 or by any other suitable means. The layer is deposited at temperatures of generally greater than about 400°C . When the base substrate is metallic, it often has a rough surface with, e.g., a RMS of 15 nm to 100 nm or greater. Generally, the inert oxide layer has a thickness of from about 100 nanometers (nm) to about 1000 nm depending upon the roughness of the base substrate with a thicker coating layer for rougher base substrate surfaces. The inert
30 oxide layer serves to provide a smooth surface for subsequent depositions. By "smooth" is

meant a surface having a root mean square (RMS) roughness of less than about 2 nm, preferably less than about 1 nm. To obtain the desired smoothness, it can be preferred to treat the deposited inert oxide layer by chemical mechanical polishing. In the case of erbium oxide, the inert oxide material can also serve as a nucleation layer for subsequent layers.

Alternatively, when using aluminum-containing metal substrates a layer of aluminum oxide can be directly formed in situ. Using aluminum-containing metal substrates with less than about 30 atomic percent aluminum has generally required a heat treatment of the metal substrate to form the aluminum oxide layer, while with aluminum-containing metal substrates containing greater than about 30 atomic percent aluminum, an intermediate aluminum oxide layer is achieved without any required heat treatment other than that achieved during normal deposition processing. Heat treatment of the aluminum-containing metal substrate generally involves heating at from about 800°C to about 1000°C in an oxygen atmosphere.

Substrates are prepared for subsequent IBAD MgO overcoatings by the following. If the as received metal alloy starts out with a RMS roughness of less than about 15 nm, the metal substrate can be chemically mechanically polished (CMP) to a RMS roughness of about 1.5 nm. (Note: For measuring roughness, all scans are done using scanning force microscopy and are over a 5 X 5 μm area.) The time needed to do this is approximately 2 minutes. The polishing slurry used is commercially available colloidal silica (e.g., Mastermet 2, 0.02 μm non-crystallizing colloidal silica suspension, available from Buehler, Ltd., Lake Bluff, Ill.). If the initial metal substrate is much rougher (e.g., a RMS roughness of greater than about 15 nm), then the metal substrate is generally mechanically polished with a 1 micron diamond paste for a short time period of from about 10 seconds to about 20 seconds to get the finish to about 4 nm to about 6 nm followed by a 2 minute CMP with silica as previously described. Preferably, the metal substrate starts out with a minimum of inclusions (less than about 5 inclusions per 5 X 5 μm area). Inclusions are usually harder than the surrounding metal matrix and generally appear as bumps or holes (where the polishing plucks them out of the metal matrix) in surface profile scans.

In one embodiment of the present invention, a layer of an amorphous oxide or oxynitride material is next deposited upon the inert oxide material layer. The amorphous oxide or oxynitride layer can serve as a nucleation layer for oriented growth of subsequent layers. The amorphous oxide or oxynitride layer can be deposited on the base substrate by pulsed laser deposition, e-beam evaporation, sputtering or by any other suitable means. The layer is generally deposited at temperatures of generally about 100°C. The amorphous oxide or oxynitride layer is typically from about 5 nm to about 100 nm in thickness, preferably from about 20 nm to about 40 nm. Among the oxide or oxynitride materials suitable as the amorphous layer are included yttrium oxide (Y_2O_3), aluminum oxynitride (AlON), erbium oxide (Er_2O_3), yttria-stabilized zirconia (YSZ), cerium oxide (CeO_2), europium oxide, nickel aluminate ($NiAl_2O_4$), and barium zirconate ($BaZrO_3$). Preferably, the layer of oxide or oxynitride amorphous material is yttrium oxide, aluminum oxynitride, erbium oxide or yttria-stabilized zirconia and more preferably is yttrium oxide or erbium oxide. For the very best surface finishes with a RMS roughness of less than about 1 nm, after the smooth or polished metal alloy is overcoated with the inert oxide film, a short (e.g., about 5 seconds) CMP step can be conducted.

In another embodiment of the invention, a single layer of erbium oxide is used to provide both the smoothness and the nucleation layer. Such a layer can be chemically mechanically polished if desired.

This intermediate article provides an excellent substrate for the subsequent deposition of a layer of an oriented cubic oxide material having a rock-salt-like structure. Such oriented cubic oxide materials can be, e.g., magnesium oxide, calcium oxide, strontium oxide, zirconium oxide, barium oxide, europium oxide, samarium oxide and other materials such as described in WO 99/25908 by Do et al. Preferably, the layer of oriented cubic oxide material having a rock-salt-like structure is a magnesium oxide (MgO) layer. Such a MgO layer is preferably deposited by electron beam evaporation with an ion beam assist. The MgO layer in the ion beam assisted deposition is typically evaporated from a crucible of magnesia. An ion-assisted, electron-beam evaporation system similar to that described by Wang et al., App. Phys. Lett., vol. 71, no. 20, pp. 2955-2957 (1997), can be used to deposit such a MgO film. Alternatively, a dual-ion-beam sputtering system similar

to that described by Iijima et al., IEEE Trans. Appl. Super., vol. 3, no. 1, pp. 1510 (1993), can be used to deposit such a MgO film. Generally, the substrate normal to ion-assist beam angle is $45 \pm 3^\circ$.

The ion source gas in the ion beam assisted deposition is argon. The ion beam
5 assisted deposition of MgO is conducted with substrate temperatures of generally from about 20°C to about 100°C. The MgO layer deposited by the IBAD process is generally from about 5 nm to about 20 nm in thickness, preferably about 8 nm to about 15 nm. After deposition of the oriented cubic oxide material having a rock-salt-like structure, e.g., MgO, an additional thin homo-epitaxial layer of the MgO can be optionally deposited by a
10 process such as electron beam or magnetron sputter deposition. This thin layer can generally be about 100 nm in thickness. Deposition of the homo-epitaxial layer by such a process can be more readily accomplished than depositing the entire thickness by ion beam assisted deposition.

A thin film template structure is also provided in accordance with the present
15 invention and includes a substrate (e.g., a polycrystalline flexible metal substrate), a layer of an inert oxide material upon the surface of the substrate, said inert oxide material layer preferably having a smooth surface (RMS roughness of less than 2 nm, preferably less than about 1 nm), a layer of an amorphous oxide or oxynitride material upon the inert oxide material layer, and, a layer of an oriented cubic oxide material having a rock-salt-like
20 structure upon the amorphous oxide or oxynitride material layer. Such a thin film template structure is useful for subsequent deposition of epitaxial thin films. Such epitaxial thin films can be formed from a material selected from the group consisting of superconductors, including high temperature superconductors, semiconductors, photovoltaic materials, magnetic materials, and precursors of superconductors or high temperature
25 superconductors. The thin film template structure is especially preferred for subsequent deposition of high temperature superconductor materials. Depending upon the particular epitaxial thin film material deposited upon the thin film template structure, additional layers such as buffer layers can be employed for enhanced chemical or structural compatibility. In the case of YBCO as a high temperature superconductor, buffer layers are
30 generally employed although they are not required.

Another thin film template structure is also provided in accordance with the present invention and includes a substrate (e.g., a polycrystalline flexible metal substrate), a layer of an inert oxide material upon the surface of the substrate, said inert oxide material layer preferably having a smooth surface (RMS roughness of less than 2 nm, preferably less than about 1 nm), and a layer of an amorphous oxide or oxynitride material upon the inert oxide material layer. Such a thin film template structure is useful as a highly smooth surface for subsequent inclined substrate deposition of thin films.

In one embodiment of the present invention, one or more intermediate layers are deposited onto the MgO layer so that they are between the MgO layer deposited by the IBAD process and the superconducting YBCO layer. The one or more intermediate layers serve as buffer layers between the MgO layer and the YBCO and assists in lattice matching. This so-called "buffer layer" should have good "structural compatibility" between the MgO or other oriented cubic oxide material deposited in the IBAD process and the YBCO and should have good chemical compatibility with both adjacent layers. By "chemical compatibility" is meant that the intermediate layer does not undergo property-degrading chemical interactions with the adjacent layers. By "structural compatibility" is meant that the intermediate layer has a substantially similar lattice structure with the superconductive material. Among the materials suitable as one or more intermediate buffer layers are cerium oxide, yttria-stabilized zirconia, strontium titanate, yttrium oxide, europium copper oxide (Eu_2CuO_4), neodymium copper oxide (Nd_2CuO_4), yttrium copper oxide (Y_2CuO_4), and other rare earth copper oxides (RE_2CuO_4) or rare earth oxides and other cubic oxide materials such as those described in U.S. Patent No. 5,262,394, by Wu et al. for "Superconductive Articles Including Cerium Oxide Layer" such description hereby incorporated by reference. In a preferred embodiment, the present invention includes a layer of yttria-stabilized zirconia or strontium titanate on the MgO layer and a top-layer of yttrium oxide or cerium oxide for the layer of yttria-stabilized zirconia. The layer of yttria-stabilized zirconia or strontium titanate is generally from about 50 nm to about 1000 nm in thickness, preferably from about 100 nm to about 500 nm in thickness. The layer of cerium oxide, yttrium oxide or strontium titanate is generally from about 5 nm to about 200 nm in thickness, preferably from about 5 nm to about 20 nm in thickness.

The intermediate or buffer layers are generally deposited at temperatures of greater than about 700°C, preferably at temperatures of from about 700°C to about 950°C.

A high temperature superconducting (HTS) layer, e.g., a YBCO layer, can be deposited, e.g., by pulsed laser deposition or by methods such as evaporation including
5 coevaporation, e-beam evaporation and activated reactive evaporation, sputtering including magnetron sputtering, ion beam sputtering and ion assisted sputtering, cathodic arc deposition, chemical vapor deposition, organometallic chemical vapor deposition, plasma enhanced chemical vapor deposition, molecular beam epitaxy, a sol-gel process, liquid phase epitaxy and the like.

10 In pulsed laser deposition, powder of the material to be deposited can be initially pressed into a disk or pellet under high pressure, generally above about 1000 pounds per square inch (PSI) and the pressed disk then sintered in an oxygen atmosphere or an oxygen-containing atmosphere at temperatures of about 950°C for at least about 1 hour, preferably from about 12 to about 24 hours. An apparatus suitable for pulsed laser deposition is
15 shown in Appl. Phys. Lett. 56, 578 (1990), "Effects of Beam Parameters on Excimer Laser Deposition of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ", such description hereby incorporated by reference.

Suitable conditions for pulsed laser deposition include, e.g., the laser, such as an excimer laser (20 nanoseconds (ns), 248 or 308 nanometers (nm)), targeted upon a rotating
20 pellet of the target material at an incident angle of about 45°. The substrate can be mounted upon a heated holder rotated at about 0.5 rpm to minimize thickness variations in the resultant film or coating. The substrate can be heated during deposition at temperatures from about 600°C to about 950°C, preferably from about 700°C to about 850°C. An oxygen atmosphere of from about 0.1 millitorr (mTorr) to about 500 mTorr, preferably from about 100 mTorr to about 250 mTorr, can be maintained within the deposition
25 chamber during the deposition. Distance between the substrate and the pellet can be from about 4 centimeters (cm) to about 10 cm.

The deposition rate of the film can be varied from about 0.1 angstrom per second ($\text{\AA}/\text{s}$) to about 200 $\text{\AA}/\text{s}$ by changing the laser repetition rate from about 0.1 hertz (Hz) to about 200 Hz. Generally, the laser beam can have dimensions of about 3 millimeters (mm) by 4

mm with an average energy density of from about 1 to 4 joules per square centimeter (J/cm^2). After deposition, the films generally are cooled within an oxygen atmosphere of greater than about 100 Torr to room temperature.

In one embodiment of the present invention illustrated in Fig. 1, a nickel alloy substrate 10 is initially coated with a layer of aluminum oxide 12 from about 80 nm to 100 nm in thickness deposited by pulsed laser deposition. The aluminum oxide layer is polished by chemical mechanical polishing to a smoothness of about 1 nm. Then, a layer 14 of Y_2O_3 of from about 5 nm to about 100 nm in thickness is deposited on the aluminum oxide by pulsed laser deposition. Then, a layer 16 of MgO (about 10 nm) is deposited on the yttrium oxide by ion beam assisted deposition. Then, a homoepitaxial layer 18 of MgO is deposited upon the IBAD-MgO layer, the homoepitaxial layer of MgO of about 100 nm in thickness deposited in a process such as electron beam or magnetron sputter deposition. Next, a first buffer layer 20 of YSZ of from about 50 nm to about 1000 nm in thickness is deposited on the MgO layer. Then a second buffer layer 22 of cerium oxide of from about 5 nm to about 40 nm in thickness is deposited on the YSZ layer. Finally, a layer 24 of YBCO is deposited, e.g., by pulsed laser deposition at a thickness of, e.g., about 1000 nm to 2000 nm.

The present invention is more particularly described in the following examples which are intended as illustrative only, since numerous modifications and variations will be apparent to those skilled in the art.

EXAMPLE 1

An ion-assisted, electron beam evaporation system similar to that of Wang et al., App. Phys. Lett., v. 71, no. 20, pp. 2955-2957 (1997), was used to deposit a MgO film upon a flexible metal substrate of Hastelloy C-276 or other nickel-based alloys. The substrates were ultrasonically cleaned in soap and water, rinsed with deionized water, rinsed with methanol and blown dry with filtered nitrogen. The ion source was manufactured by Ion Tech, Inc. (Ft. Collins, CO) with a source geometry of 22 cm by 2.5 cm. The substrate normal to ion-assist beam angle was $45 \pm 3^\circ$. The ion source gas was argon. The ion source gas was introduced to a background partial pressure of about 1.0×10^{-6} Torr with a total

pressure during deposition of about 1×10^{-4} Torr. The electron gun heated the MgO source to maintain a deposition rate of about 0.15 nm/sec. The ion-assist gun voltage and current density were about 750 eV and $100 \mu\text{A}/\text{cm}^2$ respectively.

Various amorphous oxide materials were used and x-ray phi scan measurements were taken. The results of the x-ray phi scan measurements on the final YBCO layer on the various materials are shown (full-width-half maxima) in Table 1.

TABLE 1

Amorphous oxide layer	ϕ -scan FWHM of YBCO	Buffer layer(s)	YBCO (μm)	J_c (MA/cm^2)	I_c ($\text{A}/\text{cm-width}$)
Al_2O_3	15.0	YSZ/ Y_2O_3	1.1	0.03	3
Diamond-like C	11.2	YSZ/ Y_2O_3	--	--	--
Y_2O_3	5.6	YSZ/ Y_2O_3	0.9	.05	5
Y_2O_3	5.9	SrTiO_3	0.9	0.14	13
Er_2O_3	4.0	YSZ/ CeO_2	1.1	0.86	95
YSZ (by e-beam)	5.6	YSZ/ CeO_2	1.25	0.11	14
EuO	10.5	YSZ/ CeO_2	1.25	0.03	4
Y_2O_3	4.3	YSZ/ CeO_2	1.3	0.54	70

EXAMPLE 2

On a nickel alloy substrate (Hastelloy C276), was deposited by magnetron sputter deposition a layer of aluminum oxide about 800 to about 1000 Angstroms in thickness. The aluminum oxide layer was then polished by CMP (chemical-mechanical polishing) with a colloidal suspension of silica as the polishing medium. The resultant surface of the aluminum oxide had a smoothness (RMS roughness) of about 1 nm. Onto this resultant article was deposited a layer of Y_2O_3 (about 5 nm) by e-beam evaporation. Onto this resultant article was deposited a layer of MgO about 10 nm in thickness using ion beam assisted electron beam deposition with an ion assist gas of argon. Onto the IBAD-MgO layer was then deposited a layer of homoepitaxial MgO by e-beam evaporation. Onto the top MgO layer was deposited a layer of yttria-stabilized zirconium (YSZ) about 30 nm in thickness by pulsed laser deposition. Onto the layer of YSZ was deposited a layer of cerium oxide about 30 nm in thickness by pulsed laser deposition. Finally, a layer of

YBCO about 1500 nm in thickness was then deposited on the cerium oxide by pulsed laser deposition. The J_c was measured as 1.4×10^6 A/cm² using a standard four-point measurement. The projected I_c is 210 Amperes across a sample 1 cm wide.

EXAMPLE 3

5 On a nickel alloy substrate (Haynes 242), was deposited by magnetron sputter deposition a layer of aluminum oxide about 80 nm to 100 nm in thickness. The aluminum oxide layer was then polished by CMP (chemical-mechanical polishing) with a colloidal suspension of silica as the polishing medium. The resultant surface of the aluminum oxide had a smoothness (RMS roughness) of 1 nm. Onto this resultant article was deposited a
10 layer of AlON (about 20 nm) by magnetron sputter deposition. Onto this resultant article was deposited a layer of MgO about 10 nm in thickness using ion beam assisted electron beam deposition with an ion assist gas of argon. Onto the IBAD-MgO layer was then deposited a layer of homoepitaxial MgO by e-beam evaporation. Onto the top MgO layer was deposited a layer of yttria-stabilized zirconium (YSZ) about 30 nm in thickness by
15 pulsed laser deposition. Onto the layer of YSZ was deposited a layer of cerium oxide about 30 nm in thickness by pulsed laser deposition. Finally, a layer of YBCO about 1150 nm in thickness was then deposited on the cerium oxide by pulsed laser deposition. The J_c was measured as 0.51×10^6 A/cm² using a standard four-point measurement. The projected I_c is 59 Amperes across a sample 1 cm wide.

20 Although the present invention has been described with reference to specific details, it is not intended that such details should be regarded as limitations upon the scope of the invention, except as and to the extent that they are included in the accompanying claims.

WHAT IS CLAIMED IS:

1. An article comprising:

5 a substrate;

a layer of an inert oxide material upon the surface of the substrate;

a layer of an amorphous oxide or oxynitride material upon the inert oxide material layer; and,

10 a layer of an oriented cubic oxide material having a rock-salt-like structure upon the amorphous oxide or oxynitride material layer.

2. The article of claim 1 wherein the inert oxide material layer is characterized as having a RMS roughness of less than about 2 nm.

3. The article of claim 1 further including at least one layer of a buffer material upon the oriented cubic oxide material layer.

4. The article of claim 1 further including a top-layer of YBCO upon the oriented cubic oxide material layer.

5. The article of claim 1 wherein the substrate is a flexible polycrystalline metal.

6. The article of claim 3 wherein the at least one layer of a buffer material includes a layer of a first buffer material upon the oriented cubic oxide material layer and a layer of a second buffer material upon the first buffer material layer.

7. The article of claim 3 further including a top-layer of YBCO upon the at least one layer of a buffer material.

8. The article of claim 6 further including a top-layer of YBCO upon the second buffer material layer.

9. The article of claim 1 wherein the layer of an oriented cubic oxide material having a rock-salt-like structure is deposited by ion beam assisted deposition.

10. The article of claim 9 further including at least one layer of a buffer material upon the oriented cubic oxide material layer.

11. The article of claim 10 further including a layer of homoepitaxial oriented cubic oxide material having a rock-salt-like structure between the ion beam assisted deposited cubic oxide material layer and the buffer material layer.

12. The article of claim 11 further including a top-layer of YBCO upon the at least one layer of a buffer material.

13. The article of claim 1 wherein the inert oxide material layer is a material selected from the group consisting of aluminum oxide, erbium oxide, and yttrium oxide.

14. The article of claim 1 wherein the amorphous oxide or oxynitride material layer is a material selected from the group consisting of yttrium oxide, aluminum oxynitride, erbium oxide, yttria-stabilized zirconia, cerium oxide and europium oxide.

15. The article of claim 1 wherein the oriented cubic oxide material layer is magnesium oxide.

16. The article of claim 6 wherein the first buffer material layer is yttria-stabilized zirconia.

17. The article of claim 3 wherein the at least one layer of a buffer material is strontium titanate.

18. The article of claim 6 wherein second buffer material layer is a material selected from the group consisting of cerium oxide, yttrium oxide, europium copper oxide, neodymium copper oxide, yttrium copper oxide, other rare earth oxides and other rare earth copper oxides.

19. An article comprising:

a substrate;

a layer of an amorphous oxide or oxynitride material upon the surface of the substrate;

and,

5 a layer of an oriented cubic oxide material having a rock-salt-like structure upon the amorphous oxide or oxynitride material layer.

20. The article of claim 19 wherein the layer of an amorphous oxide or oxynitride material is characterized as having a RMS roughness of less than about 2 nm.

21. The article of claim 19 further including at least one layer of a buffer material upon the oriented cubic oxide material layer.

22. The article of claim 19 further including a top-layer of YBCO upon the oriented cubic oxide material layer.

23. The article of claim 19 wherein the substrate is a flexible polycrystalline metal.

24. The article of claim 21 wherein the at least one layer of a buffer material includes a layer of a first buffer material upon the oriented cubic oxide material layer and a layer of a second buffer material upon the first buffer material layer.

25. The article of claim 24 further including a top-layer of YBCO upon the at least one layer of a buffer material.

26. The article of claim 24 further including a top-layer of YBCO upon the second buffer material layer.

27. The article of claim 19 wherein the layer of an oriented cubic oxide material having a rock-salt-like structure is deposited by ion beam assisted deposition.

28. The article of claim 27 further including at least one layer of a buffer material upon the oriented cubic oxide material layer.

29. The article of claim 28 further including a layer of homoepitaxial oriented cubic oxide material having a rock-salt-like structure between the ion beam assisted deposited cubic oxide material layer and the buffer material layer.

30. The article of claim 19 wherein the amorphous oxide material layer is erbium oxide.

31. The article of claim 19 wherein the oriented cubic oxide material layer is magnesium oxide.

32. A thin film template structure for subsequent epitaxial thin film deposition comprising:

a polycrystalline flexible metal substrate;

a layer of an inert oxide material upon the surface of the polycrystalline flexible metal substrate;

a layer of an amorphous oxide or oxynitride material upon the inert oxide material layer; and,

a layer of an oriented cubic oxide material having a rock-salt-like structure upon the amorphous oxide or oxynitride material layer.

33. The thin film template structure of claim 32 wherein the inert oxide material layer is characterized as having a RMS roughness of less than about 2 nm.

34. The thin film template structure of claim 32 wherein the inert oxide material layer is a material selected from the group consisting of aluminum oxide, yttrium oxide, and erbium oxide.

35. The thin film template structure of claim 32 wherein the amorphous oxide material layer is a material selected from the group consisting of yttrium oxide, aluminum oxynitride, erbium oxide, yttria-stabilized zirconia, cerium oxide and europium oxide.

36. The thin film template structure of claim 32 wherein the oriented cubic oxide material layer is magnesium oxide.

37. The thin film template structure of claim 32 further including a layer of a first buffer material upon the oriented cubic oxide material layer.

38. The thin film template structure of claim 37 wherein the buffer layer is a material selected from the group consisting of yttria-stabilized zirconia and strontium titanate.

39. The thin film template structure of claim 37 further including a layer of a second buffer material upon the layer of a first buffer material.

40. The thin film template structure of claim 39 wherein the second buffer layer is a material selected from the group consisting of cerium oxide, yttrium oxide, europium copper oxide, neodymium copper oxide, yttrium copper oxide, other rare earth copper oxides and other rare earth oxides.

41. A thin film template structure for subsequent epitaxial thin film deposition comprising:

a polycrystalline flexible metal substrate;

5 a layer of an inert oxide material upon the surface of the polycrystalline flexible metal substrate; and,

a layer of an amorphous oxide or oxynitride material upon the inert oxide material layer.

42. The thin film template structure of claim 41 wherein the inert oxide material layer is characterized as having a RMS roughness of less than about 2 nm.

43. The thin film template structure of claim 41 wherein the inert oxide material layer is a material selected from the group consisting of aluminum oxide, yttrium oxide, and erbium oxide.

44. The thin film template structure of claim 41 wherein the amorphous oxide material layer is a material selected from the group consisting of yttrium oxide, aluminum oxynitride, erbium oxide, yttria-stabilized zirconia, cerium oxide and europium oxide.

1/1

YBCO	24
CeO ₂	22
YSZ	20
Homoepitaxial MgO	18
IBAD MgO	16
Y ₂ O ₃	14
Al ₂ O ₃	12
Ni alloy substrate	10

Fig. 1

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
13 June 2002 (13.06.2002)

PCT

(10) International Publication Number
WO 02/047119 A3

(51) International Patent Classification⁷: B21D 39/00,
H01B 12/00, H01F 6/00, H01L 39/00

(21) International Application Number: PCT/US01/46877

(22) International Filing Date: 4 December 2001 (04.12.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/731,534 6 December 2000 (06.12.2000) US

(71) Applicant: THE REGENTS OF THE UNIVERSITY
OF CALIFORNIA [US/US]; Los Alamos National Labo-
ratory, LC/IP, MS A187, Los Alamos, NM 87545 (US).

(72) Inventors: ARENDT, Paul, N.; 411 Richard Court, Los
Alamos, NM 87544 (US). FOLTYN, Stephen, R.; 1
Mariposa Court, Los Alamos, NM 87544 (US). GROVES,
James, R.; 2426-A 35th Street, Los Alamos, NM 87544
(US). HOLESINGER, Terry, G.; 2783-A Walnut Street,
Los Alamos, NM 87544 (US). JIA, Quanxi; 832 Kristi
Lane, Los Alamos, NM 87544 (US).

(74) Agents: COTTRELL, Bruce, H. et al.; Los Alamos
National Laboratory, LC/IP, MS A187, Los Alamos, NM
87545 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM,
HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK,
LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX,
MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL,
TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR,
GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent
(BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR,
NE, SN, TD, TG).

Published:

— with international search report

(88) Date of publication of the international search report:
12 December 2002

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: HIGH TEMPERATURE SUPERCONDUCTING THICK FILMS FIELD OF THE INVENTION

YBCO	24
CeO ₂	22
YSZ	20
Homoepitaxial MgO	18
IBAD MgO	16
Y ₂ O ₃	14
Al ₂ O ₃	12
Ni alloy substrate	10

(57) Abstract: An article including a substrate (10), a layer of an inert oxide material (12) upon the surface of the substrate (10), a layer (14) of an amorphous oxide or oxynitride material upon the inert oxide material layer (12), a layer of an oriented cubic oxide material (16) having a rock-salt-like structure upon the amorphous oxide material layer (14) is provided together with additional layers such as at least one layer of a buffer material (20, 22) upon the oriented cubic oxide material layer (16) or a HTS top-layer (24) of YBCO directly upon the oriented cubic oxide material layer (16). With an HTS top-layer (24) of YBCO upon at least one layer of a buffer material (20, 22) in such an article, Jc's of 1.4 X 10⁶ A/cm² have been demonstrated with projected Ic's of 210 Amperes across a sample 1 cm wide.

WO 02/047119 A3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/46877

A. CLASSIFICATION OF SUBJECT MATTER		
IPC(7) : B21D 39/00; H01B 12/00; H01F 6/00; H01L 39/00		
US CL : 505/812, 813, 814, 238, 237; 428/621, 622, 623, 627, 629, 632, 930		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) U.S. : 505/812, 813, 814, 238, 237; 428/621, 622, 623, 627, 629, 632, 930		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WEST		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,527,766 A (EDDY) 18 June 1996 (18.06.1996).	1-44
A,P	US 6,190,752 B1 (DO et al.) 20 February 2001 (20.02.2001).	1-44
A	US 5,912,068 A (JIA) 15 June 1999 (15.06.1999).	1-44
A	US 5,798,903 A (DHOTE et al.) 25 August 1998 (25.08.1998).	1-44
A	US 4,828,664 A (DIETRICH et al.) 9 May 1989 (09.05.1989).	1-44
A	US 4,657,776 A (DIETRICH et al.) 14 April 1987 (14.04.1987).	1-44
A	US 4,581,289 A (DIETRICH et al.) 8 April 1986 (08.04.1986).	1-44
A	US 4,238,232 A (MINOMURA) 9 December 1980 (09.12.1980).	1-44
A	US 4,225,409 A (MINOMURA) 30 September 1980 (30.09.1980).	1-44
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents:		
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	
"E" earlier application or patent published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family	
"P" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search 28 February 2002 (28.02.2002)	Date of mailing of the international search report 22 MAR 2002	
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703)305-3230	Authorized officer Thomas Dunn Telephone No. 703-308-0661	